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LUBRICATING OIL CONTAINING DICYCLOPENTADIENYL IRON AND AN OIL SOLUBLE ORGANIC DIVALENT METAL SALT

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This invention relates to lubricants for use in knock-inducing engines such as spark-ignition internal combustion engines. More particularly, this invention pertains to lubricating compositions possessing knock-reducing detergent and anti-wear properties.

In many instances it has been found desirable to add an anti-knock agent to a lubricant to act in an auxiliary capacity with a knock-inhibited fuel such as fuels containing tetraethyl lead with or without tricresylphosphate, triphenylphosphate, tributylphosphate, in order to economically and effectively increase octane requirement or aid in overcoming the maldistribution problem generally encountered in multi-cylinder engines.

Although ferrocene (dicyclopentadienyl iron) and ferrocene compounds, when added in minor amounts to lubricating oils, effectively act in the manner described above and in addition, often impart a carryover anti-knock effect in cases where ordinary fuels are used later, however, ferrocene compounds have the disadvantage of causing wear.

It has been found that lubricating compositions of this invention which contain minor, but knock-inhibiting amounts of a ferrocene compound can be effectively inhibited against wear by addition thereto of a minor amount, generally less than about 5% by weight of oil-soluble metal salts of organic acidic compounds and/or inorganic acidic compounds containing an organic radical such as metal carboxylates, naphthenates, carbamates, sulfonates, phenates, alcoholates, phosphates, phosphonates and including the thio analogues. The anionic portion of said salts can contain various substituent groups such as halogens, amino, cyano, alkyl, cycloalkyl, radicals and the like. Preferred compounds are the metal sulfonates and/or phenates.

The discovery that these salts which normally function as detergents or corrosion inhibitors when used in combination with ferrocene compounds as will be herein described can act as wear-inhibitors is most unexpected since normally salts in general do not possess wear-inhibiting properties.

Ferrocene, $Fe(C_5H_5)_2$, also known as dicyclopentadienyl iron, and the preparation thereof, have been described by T. J. Kealy, and T. L. Pauson, Nature, vol. 168 (1951) p. 1040. Also, R. B. Woodward et al., J. A. C. S. vol. 74 (1952) p. 3458, have described the preparation of various derivatives of ferrocene. Other ferrocene compounds include substituted ferrocenes such as acrylated, carboxylated, halogenated, alkylated, aminated and alcoholated ferrocenes, and the like. Thus, diacetylferrocene, ferrocene, dicarboxylic acid, bis-(β-chloropropionyl) ferrocene, diacryloylferrocene, dichloroferrocene, tetrachloroferrocene, diaminoferrocene, dihydroxyferrocene, diethoxyferrocene, dimethylferrocene, diethylferrocene, tetraethylferrocene, diisopropylferrocene, di-n-propylferrocene, dibutylferrocene, di-n-butylferrocene, dioctylferrocene, monopropylmonobutylferrocene, and other substituted ferrocenes are excellent anti-knock agents, when utilized in lubricating oils.

The second essential additive in lubricating compositions of this invention include oil-soluble salts (metal and non-metal) of organic acidic compounds or inorganic acids containing organic radicals such as alkali, alkaline earth and heavy metal salts of carboxylic acids, sulfonic acids, naphthenic acids, carbamic acids, phenolic compounds, organic acid phosphates, phosphonic acids and the thio analogues of said acidic compounds. Preferred are the oil-soluble polyvalent metal sulfonates and phenates such as the Ca, Ba, Mg, Al, Zn and Pb petroleum sulfonate, naphthenate and alkyl phenates.

The sulfonates for use in compositions of this invention include petroleum sulfonates described in U. S. Patents 2,280,419, 2,344,988, 2,361,804, 2,375,222, 2,480,638, 2,485,861, 2,509,863, 2,501,731, 2,523,582, and 2,585,520. If desired, the sulfonates can be purified by the methods described in United States Patents 2,441,258 and 2,488,721. The aromatic sulfonates which can be utilized in compositions of this invention include those described in United States Patents 2,411,583, 2,418,894, 2,442,915, 2,483,501, 2,531,325, 2,556,198 and 2,556,848. Although various metal sulfonates are contemplated in the practice of the invention, including alkali metal sulfonates, alkaline earth metal sulfonates (including magnesium) and other polyvalent metal sulfonates, particularly other divalent metal sulfonates and trivalent metal sulfonates, the sulfonates, the sulfonates of the metals of Group II of the Periodic Table and having an atomic number from 12 to 56 are preferred, and especially of the alkaline earth metals within that group of metals. Specific sulfonates which are particularly suitable for use in compositions of this invention include oil-soluble metal sulfonates such as Na, K, Li, Ca, Ba, Mg, Zn, Al, Zn, Sn, Cr and Co petroleum sulfonate, tetra-tertiary butyl naphthalene sulfonate, diwax benzene sulfonate, stearyl benzene sulfonate, diwax naphthalene sulfonate, diisobutylene phenol sulfonate, tertiary octyl phenol sulfonate, di-tertiary amyl phenol sulfonate, alkylated dibenzothiophene sulfonate and mixtures thereof.

The phenates suitable for use in compositions of this invention include those described in United States Patents 2,197,833, 2,228,654, 2,280,419, 2,344,988, 2,361,804, 2,410,652, 2,501,991, 2,501,992, and 2,610,982. Specifically, they can be either simple phenates such as metal alkylphenates (Ca cetylphenate), polar substituted simple phenates (Ca or Zn alkylsalicylates) or polyphenates such as where a plurality of the simple phenates are condensed at positions ortho and/or para to the phenolic hydroxy group through alkylidene (methylene) radicals or other suitable divalent non-metallic radicals, such as sulfur or selenium. Although various metal phenates are contemplated in the practice of the invention including mono- and polyvalent metal phenates, such as the alkali, alkaline earth and heavy metal phenates of which preferred are the polyvalent metal phenates of the metals of Group II of the Periodic Table and having an atomic number from 12 to 56, especially the alkaline earth metals within that group of metals. Illustrative compounds are: Na, K, Li, Ca, Ba, Sr, Mg, Zn, Al, Cd, Ni, Fe, Co cetyl phenate, dibutyl phenate, C_{14}–C_{18} salicylate, octyl thiophenate, cyclohexyl phenate, cetyl phenol sulfide, waxyl phenate, as well as the above metal salts of the condensation product of alkyl phenol with formaldehyde, acetaldehyde or benzaldehyde, e. g., Ca, Ba or Mg salts of octyl phenol-formaldehyde condensation product ranging in molecular weight of from 500 to 1,100.

Although the above salts are preferred oil-soluble sodium, calcium, barium, zinc, lead, aluminum, salts of alicyclic acid, e. g., naphthenic acid, fatty acids such as oleic, stearic, phenyl mercapto stearic; aromatic acids, e. g., dibutyl phthalic acid, dioctyl benzoic acid; nitrogen-containing acids, e. g., dibutyl dithiocarbamic acid; or-

ganic phosphorus-containing acids, e. g., di(methylcyclohexyl) dithiophosphate, butyl trichloromethane phosphonic acid and the like can be used in place of the sulfonates and/or phenates described above or in combination therewith.

The quantities of each of the anti-knock compounds and the salts which can be incorporated into the present base compositions such as lubricating oils or fuels will depend somewhat upon the particular anti-knock compound used, the engine in which the material is to be utilized and the degree anti-knock requirement desired to be met. In general, an effective amount of each of said additives for use in lubricating oils can vary from about 0.01% to about 10% and preferably can vary from about 0.1% to about 5% by weight or as low as 0.05% and even 0.01% by weight.

The base oil of this invention in general will be a mineral lubricating oil, but various natural or synthetic liquid materials having suitable lubricating properties are suitable for use in the compositions of the invention. Thus, the base may be a hydrocarbon oil including the paraffinic, naphthenic types as well as mixtures thereof. The viscosity of these oils may vary over a wide range such as from 45 SUS to 100° F. to 100 SUS at 210° F. The hydrocarbon oils may be blended with fixed oils such as castor oil, lard oil and the like and/or with synthetic lubricants such as polymerized olefins, copolymers of alkylene glycols and alkylene oxides, organic esters, e. g., 2-ethylhexyl sebacate, dioctyl phthalate; polymeric tetrahydrofuran, polyalkyl silicone polymers, e. g., dimethyl silicone polymer and the like. If desired, the synthetic lubricants may be used as the sole base lubricant or as the predominant base component or admixed with fixed oils and derivatives thereof.

Compositions of this invention are illustrated by the following examples:

Composition A

Ferrocene	percent wt. 0.5
Ca petroleum sulfonate	percent SA[1] 0.4
Mineral lubricating oil	Essentially balance

Composition B

Dibutyl ferrocene	percent wt. 0.5
Ca petroleum sulfonate	percent SA 1.0
Mineral lubricating oil	Essentially balance

Composition C

Dibutyl ferrocene	percent wt. 4.3
Ca petroleum sulfonate	percent SA 0.4
Ca salt of octyl phenol-formaldehyde condensation product (M. W. 900–1100)	percent SA 0.3
Mineral lubricating oil	Essentially balance

Composition D

Dipropyl ferrocene	percent wt. 0.5
Ca petroleum sulfonate	percent SA 0.4
Ca salt of octyl phenol-formaldehyde condensation product (M. W. 900)	percent SA 0.3
Phenol-α-naphthylamine	percent wt. 0.2
Mineral lubricating oil	Essentially balance

Composition E

Dibutyl ferrocene	percent wt. 8.7
Ca naphthenate	percent wt. 3.0
Mineral lubricating oil	Essentially balance

Composition F

Ferrocene	percent wt. 1.5
Zinc di(methyl cyclohexyl)dithio phosphate	percent wt. 0.2
Mineral lubricating oil	Essentially balance

Composition G

Dibutyl ferrocene	percent wt. 4.0
Ca stearate	percent wt. 2.0
Mineral lubricating oil	Essentially balance

Composition H

Ferrocene	percent wt. 1.0
Ca petroleum sulfonate	percent wt. 2.0
Ca naphthenate	percent wt. 2.0
Mineral lubricating oil	Essentially balance

Composition I

Dibutyl ferrocene	percent wt. 0.5
Ca petroleum sulfonate	percent SA 1.0
Di-2-ethyl hexyl sebacate	Essentially balance

Composition J

Diamyl ferrocene	percent wt. 2.0
Ba petroleum sulfonate	percent wt. 1.0
Mineral lubricating oil	Essentially balance

Composition K

Ferrocene	percent wt. 1.0
Ca polyalkyl benzoate	percent wt. 1.0
Mineral lubricating oil	Essentially balance

[1] SA = Sulfate Ash.

Compositions A through K showed an octane benefit varying from 2 to 18 octane numbers when tested in the CFR and Lauson engines using a primary fuel and in field tests using both a primary and secondary reference fuel. Compositions A, B, C and D were also tested in the CFR and Lauson engines for wear reducing effects and wear was reduced by from 25% to 75% over a base lubricating oil or lubricating oils containing only about 1.2% ferrocene.

Compositions of this invention are particularly effective when used in combination with primary fuels such as fuels containing tetraethyl lead (TEL), iron carbonyl, with or without the added presence of organic phosphates such as a tricresylphosphate, triphenylphosphates, triethylphosphites, or various combustion chamber deposit inhibitors, pre-ignition agents, spark plug anti-foulants, anti-oxidents, and the like.

We claim as our invention:

1. A lubricating oil composition comprising a predominant amount of a lubricating oil and a minor, but effective knock-reducing amount of a dicyclopentadienyl iron compound containing only iron, carbon and hydrogen in the molecule, and a minor, but effective, wear-inhibiting amount of an oil-soluble divalent metal salt of an organic acidic compound selected from the group consisting of divalent metal sulfonates, divalent metal phenates, divalent metal phosphates and divalent metal carboxylates.

2. A lubricating oil composition comprising a predominant amount of a lubricating oil and a minor, but effective, knock-reducing amount of an alkyl dicyclopentadienyl iron and a minor, but effective, wear-inhibiting amount of an oil-soluble divalent metal sulfonate.

3. A lubricating oil composition comprising a predominant amount of a lubricating oil and a minor, but effective, knock-reducing amount of an alkyl dicyclopentadienyl iron and a minor, but effective, wear-inhibiting amount of an oil-soluble divalent metal phenate.

4. A lubricating oil composition comprising a predominant amount of a mineral lubricating oil and a minor, but effective, knock-reducing amount of dicyclopentadienyl iron and a minor, but effective, wear-inhibiting amount of an oil-soluble divalent metal sulfonate.

5. A lubricating oil composition comprising a predominant amount of a mineral lubricating oil and a minor, but effective, knock-reducing amount of dicyclopentadienyl iron and a minor, but effective, wear-inhibiting amount of an oil-soluble divalent metal phenate.

6. A lubricating oil composition comprising a pre-

dominant amount of a mineral lubricating oil and a minor, but effective, knock-reducing amount of dicyclopentadienyl iron and a minor, but effective, wear-inhibiting amount of an oil-soluble divalent metal naphthenate.

7. A lubricating oil composition comprising a predominant amount of a mineral lubricating oil and a minor, but effective, knock-reducing amount of dicyclopentadienyl iron and a minor, but effective, wear-inhibiting amount of an oil-soluble divalent metal phosphate.

8. A lubricating oil composition comprising a predominant amount of a mineral lubricating oil and a minor, but effective, knock-reducing amount of dicyclopentadienyl iron and a minor, but effective, wear-inhibiting amount of an oil-soluble alkaline earth metal sulfonate.

9. A lubricating oil composition comprising a predominant amount of a mineral lubricating oil and a minor, but effective, knock-reducing amount of dicyclopentadienyl iron and a minor, but effective, wear-inhibiting amount of an oil-soluble alkaline earth metal phenate.

10. A lubricating oil composition comprising a predominant amount of a mineral lubricating oil and a minor, but effective, knock-reducing amount of dicyclopentadienyl iron and a minor, but effective, wear-inhibiting amount of an oil-soluble alkaline earth metal naphthenate.

11. A lubricating oil composition comprising a predominant amount of a mineral lubricating oil and a minor, but effective, knock-reducing amount of dicyclopentadienyl iron and a minor, but effective, wear-inhibiting amount of an oil-soluble alkaline earth metal phosphate.

12. A lubricating oil composition comprising a predominant amount of a mineral lubricating oil and a minor, but effective, knock-reducing amount of dibutyl dicyclopentadienyl iron and a minor, but effective, wear-inhibiting amount of an oil-soluble Ca petroleum sulfonate.

13. A lubricating oil composition comprising a predominant amount of a mineral lubricating oil and a minor, but effective, knock-reducing amount of dicyclopentadienyl iron and a minor, but effective, wear-inhibiting amount of an oil-soluble alkaline earth metal salt of octyl phenol-formaldehyde condensation product and of an oil-soluble alkaline earth metal sulfonate.

14. A lubricating oil composition comprising a predominant amount of a mineral lubricating oil and a minor, but effective, knock-reducing amount of dibutyl dicyclopentadienyl iron and a minor, but effective, wear-inhibiting amount of an oil-soluble alkaline earth metal salt of octyl phenol-formaldehyde condensation product and of an oil-soluble alkaline earth metal sulfonate.

15. A lubricating oil composition comprising a predominant amount of a mineral lubricating oil and a minor, but effective, knock-reducing amount of dibutyl dicyclopentadienyl iron and minor, but effective, wear-inhibiting amounts of an oil-soluble Ca of octyl phenol-formaldehyde condensation product and Ca petroleum sulfonate.

16. A lubricating oil composition comprising a predominant amount of a lubricating oil and a minor, but effective, knock-reducing amount of an alkyl dicyclopentadienyl iron and a minor, but effective, wear-inhibiting amount of an oil-soluble divalent metal naphthenate.

17. A lubricating oil composition comprising a predominant amount of a lubricating oil and a minor, but effective, knock-reducing amount of an alkyl dicyclopentadienyl iron and a minor, but effective, wear-inhibiting amount of an oil-soluble divalent metal phosphate.

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